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SYNOPSIS

The effect of water vapor on a polyimide has been investigated in the temperature region -190° to 325°C using an automated torsion pendulum. A damping peak "T_{H_2O}" develops at -122°C (1 Hz) in the thermomechanical spectra of the polymer which is due to water-polymer interactions. The peak intensifies as the humidity of the conditioning atmosphere, at both 30°C and at 325°C, increases and attains a limiting value at about 2000 ppm_v H_2O. The process is reversible. It is concluded that the number of sites in the polymer for interaction with water is low and limited ($<$ 0.3 molecules H_2O per polymer repeat unit) and, assuming direct proportionality between the intensity of the loss peak and the amount of water adsorbed, that the adsorption of water vapor follows the Langmuir isotherm. (Author).

-2-

INTRODUCTION

Water molecules associate strongly with polar polymers through hydrogen bond formation (1), the exothermic heat of formation of which is in the range 3.4 to 6.6 Kcal/mole (2-4).

Recent publications (5, 6) have reported that a water sensitive damping peak "T_{H_2O}" appears in the thermomechanical spectra of polyimides obtained using the torsional braid analysis (TBA) technique (7). This damping peak is in the temperature range -90° to -120°C and varies with the molecular structure of the polyimides (6). In epoxy systems (8, 9), T_{H_2O} appears at higher temperatures (ca. -70°C) on the shoulder of a glassy state transition (T_{sec} = ca. -90°C); both transitions are coupled. The T_{H_2O} damping peak in polymethylmethacrylates (10,11) at ca. - 100°C is also on the shoulder of a glassy state transition [T_{sec} = 24°C (1.24 Hz)] and increases in intensity with the humidity level of the conditioning atmosphere. In polyaminoacids (12), two types of T_{H_2O} peaks were reported, at -120° to -130°C and at 0° to 35°C. Table 1 summarizes results obtained earlier in this laboratory. The effect of water on natural products, such as lecithin and human erythrocyte ghosts, has been investigated elsewhere using TBA (13). High amounts of water in these materials (66-100%) produced large differences between the wet and dry materials; distinct peaks developed in the vicinity of -120°, -25° and 35°C due to the presence of water.

Since the locations of T_{H_2O} varies with polymer structure, it may be concluded that the relaxations are due to specific associations of water molecules with polymeric materials and not merely to condensation of water on the surface of the materials.

The particular polyimide system examined in this work (Fig. 1) is especially suitable for investigating the water vapor effect since the T_{H_2O} damping peak is isolated from T_{sec} and is symmetric.

Linear aromatic polyimides are formed usually from the reactions of dianhydrides of tetracarboxylic acids with diamines. When the dianhydride is treated in solution with the diamine at room temperature, a polyamic acid is formed; heating yields the polyimide (imidization). If the polyamic acid formation stage is undesirable, a tetraacid can be used in place of dianhydride; the two stages of the reaction then occur together by heating or by adding another anhydride (usually acetic anhydride) to the reaction mixture (Fig. 1). The high glass transition temperatures of the high temperature polyimides, the low extents of softening which occur through their glass transition temperatures, and the thermal reactions which stiffen the materials on heating above the glass transitions, prevent processing by conventional thermoplastic methods. They are therefore formed in the fabrication process from reactive precursors, imidization being completed *in situ*.

The current report deals with a recently introduced commercial system (duPont NR-150A2) which is outlined in Fig. 1 (14). In particular, an attempt has been made to correlate the intensity of the H_2O damping peak of the polyimide to the level of water vapor and to the temperature of the conditioning atmosphere.

EXPERIMENTAL

Materials and Sample Preparation

The precursor solution was made from a stoichiometric mixture of the 6F tetraacid [2,2-bis(3',4'-dicarboxyphenyl) hexafluoropropane] and 4,4'-oxydianiline dissolved in a 3:1 mixture by weight of N-methyl pyrrolidone and ethanol. A composite specimen of polymer precursor and glass braid was utilized for the torsion pendulum studies. After mounting a solution-impregnated braid, solvent was removed from the specimen and the imidization reactions were completed in the TBA apparatus *in situ* in He by heating the specimen to 325°C for 5 hours. After cure, the composite specimen contained 48% by weight of polymer. The intrinsic viscosity of such a polymer in H_2SO_4 (conc.) at 25°C is about 0.8 dl/g (14, 15).

Instrumentation and Data Representation

TBA: Thermomechanical TBA spectra were obtained using a fully automated torsion pendulum analysis system (7, 16, 17, 18). A hard-wired analog computer (data reducer) (17, 18) provided automatic alignment of the transducer, initiation of oscillations of the pendulum, printing of the values of the temperature (mV, from an iron-constantan thermocouple), period (P in sec.) and logarithmic decrement (Δ) of the damped oscillations. [$\Delta = (1/n)\ln (A_i/A_{i+n})$, where A_i is the amplitude of deformation of the ith oscillation and n is the number of oscillations between two fixed arbitrary boundary amplitudes in each wave]. The reduced data were also presented on an XY recorder versus the temperature (or time) as the logarithm

of the relative rigidity ($1/P^2$) [which is a good approximation (19) for the relative elastic shear modulus (G')] and the logarithm of Δ.

Constant and different levels of water vapor in the atmosphere were obtained by mixing wet and dry gas streams of He (8). The levels of water were measured by an electronic hygrometer in the outlet port of the apparatus and ranged from 20 to 10,000 ppm_v (parts per million on a volume basis) of H_2O in He.

TGA and DTA measurements were recorded on a duPont 950 Thermogravimetric Analyzer and on a duPont 900 Differential Thermal Analyzer. The precursor solution was used "as received".

Experiments

TBA: A single specimen was used. The uncured specimen was heated to 325°C at a rate of 1.5°C/min (the rate used in all the TBA experiments) and post-cured by continued heating for 5 hours at 325°C in 20 ppm_v H_2O/He in order to provide a specimen which would be chemically inert at 325°C. A spectrum of the "dry" specimen was then recorded on decreasing and then on increasing the temperature (325° → -190° → 325°C) in order to check reversibility of the data. The specimen was conditioned at 325°C at a constant level of water vapor for a measured time and the spectrum was recorded, using the same input atmosphere used for conditioning, again in the two directions of change in the temperature (325° → -190° → 325°C) in order to investigate hysteresis phenomena (including the effect of condensation of water on the specimen). The specimen was cooled to 30°C, conditioned at the same level of water vapor and period of time and then a plot was taken (30° → -190°C → 30°C) again using the input atmosphere used for conditioning the specimen. The temperature was then increased to 325°C and a new cycle

-6-

with a different level of water vapor was undertaken.

Below 0°C water freezes on the walls of the apparatus, and the level of water vapor in the atmosphere around the specimen decreases (Fig. 2). However, the amount of   trapped water in the polymer remains unchanged (8). As the temperature is raised through 0°C the condensed water evaporates thus increasing the level of water in the atmosphere; at higher temperatures it decreases to the original level. Since the polymer was exposed to high humidity during this process, the specimen was heated to 325°C in order to eliminate water prior to reequilibration with a different level of water vapor.

TGA: Prepolymer solution ($\sim$ 8 mg) was used "as received". The relative weight was recorded versus temperature to 325°C in N_2 (5 ppm_v H_2O). At 325°C, an isothermal experiment was run for 135 min. and then the sample was heated to 750°C (Fig. 5, $\Delta T/\Delta t$ = 5°C/min).

RESULTS AND DISCUSSION

Cure

The thermomechanical data of Fig. 3 show the changes which occur on heating the unreacted "as received" material to 325°C. It is evident that the removal of solvents and the imidization reaction proceed rapidly in the vicinity of 170°C. This is in accord with other experiments (14, 15).

After the above cure, the transitions were (Fig. 3): T_g = 313°C (0.62 Hz), T_{sec} = 135°C broad (1.0 Hz), T_{H_2O} = -117°C (1.1 Hz). The latter (T_{H_2O}) relaxation is not observed after post-curing at 325°C for 5 hours in a dry atmosphere (20 ppm_v H_2O/He) (Fig. 4), but reappears after exposure to water vapor (Fig. 6). After the post-cure, the T_g had risen to 319°C (0.61 Hz)

but T_{sec} was unchanged. Another glassy state relaxation, T < -190°C, is apparent in the dry material (Fig. 4). Hysteresis is observed immediately below T_g (Fig. 4).

The reported T_g [285°C (14)] is lower than the present results due to the undercure of the different thermal treatments. TGA experiments (Fig. 5) show that a small loss of weight occurs particularly during the first 2 hours of postcure at 325°C. The polymer is then stable to above 500°C.

The thermomechanical behavior of the polyimide is consistent with previous investigations (5, 6). As expected, the damping curve of the polyimide is similar to those of polyimides derived from benzophenone tetracarboxylic acid and from $[(COOH)_2C_6H_3]_2Si(CH_3)_2$ with 4,4'-oxydianiline (Table 2, polymers 3 and 4). In these three cases the spectra consist of sharp T_g and broad T_{sec} transitions. Although T_g depends on the specific structure of the polymer, the ratio T_{sec}/T_g (°K/°K) is unchanged (0.68 - 0.70) for both the reported and for the present work. A water-sensitive loss peak in the vicinity of -100°C is also observed in the three polymers.

Incorporation of the perfluoroisopropylidene group between the aromatic rings results in increased chain flexibility over that of pyromellitic dianhydride (PMDA). However, motion between the two aromatic rings of the tetraacid is restricted by the trifluoromethyl groups in comparison with the effect of the carbonyl and $Si(CH_3)_2$ linkages. The result is a higher T_g than for polymers 3 and 4, but lower than for the more rigid polymer 1 (Table 2).

Effect of Water

When water vapor is introduced in the atmosphere a "T_{H_2O}" peak at (e.g. Fig. 6) $-122° \pm 2°C$ (1.0 -1.1 Hz) emerges in the polyimide spectra. According to previous publications (5, 6), T_{H_2O} appears in polyimide spectra even when the atmosphere is "dry". Water elimination was effected in some of the polymers only when the polyimide was heated overnight at 130°C (i.e. below T_g) (e.g. Table 1, polymer 1). Drying could be accomplished with the presently examined polyimide only by heating above the T_g of the polymer [where diffusion is facilitated (20)].

Experimental results showing the T_{H_2O} transition versus level of water vapor in the conditioning atmosphere at 30°C are summarized in Fig. 7 and Fig. 8. (The time for equilibration was found to be less than 1 hour at 30°C.) The peak is isolated from T_{sec} and does not affect T_g and T_{sec}. Since it is also symmetric and its location is not affected by its intensity (Table 3), the observance of its change as a function of the external humidity is simplified. Its intensity reaches a limiting value in the vicinity of levels of 2000 ppm H_2O.

When a humid atmosphere is introduced into the TBA apparatus at temperatures below the frost point of water (on heating or cooling), T_{H_2O} does not appear (8, 9). Thus, it is concluded that T_{H_2O} is due to polymer-water interactions and not simply to an intrinsic property of condensing water. This interaction is probably caused by hydrogen bonding (which is observed in the IR spectra of the polyimide (15)].

The maximum capacity of water in the polymer, assuming five binding sites per repeat unit, is 12.9% (wt. water/wt. "moist" polymer). The actual take-up of water in the plateau region after conditioning at 30°C

was found to be less than 1% by weight measurement. This low water absorption agrees with results of other workers (14, 15). The low pick-up of water is related to the hydrophobic character of the polymer which contains six fluorine atoms and four aromatic groups in each repeat unit. The reversibility of the water effect is apparent from a comparison of Figures 9 and 4. When the polymer was dried, the peak at T_{H_2O} diminished almost to the original intensity.

From the present results it is difficult to conclude whether the effect is a surface or a bulk phenomenon. Nevertheless, two observations support the nature of water diffusion in bulk:

a) The time (5 hr) needed to dry the polymer and the necessity to heat it above T_g (325°C) for that purpose.

b) When the polyimide was fabricated with a low void content (low surface area) no marked differences in the water content were observed (14).

Two different temperatures for conditioning were chosen, one above the glassy state (325°C) and one close to room temperature (30°C). The specimen was conditioned at the desired level of water vapor and temperature for one hour. Longer times (5 hr) did not affect the results. As is seen in Fig. 8, larger values of Δ were obtained at 30°C than at 325°C for low levels of water vapor (up to ca. 2000 ppm H_2O/He). At higher levels of water vapor, the same plateau value for Δ was reached for both temperatures. Since the equilibration time is relatively short, a reequilibration occurs as the temperature decreases to 30°C during the thermomechanical experiment. Therefore the real difference of the water pick up at these two temperatures should be higher than that observed. The additional thermal hysteresis in the temperature region 190°C to 280°C (cf.Fig. 4 and Fig. 6) provides supporting evidence for polymer-water interactions, even in the high temperature region. Because of the low pick-up of water and the low retention of it at high temperatures,

no significant decrease of T_g could be observed on account of plasticization by water.

In previous investigations on epoxy systems (8), it has been shown that higher absorbance of water at low temperatures, as in the present system, supports a theory of bond formation between water and the polymer rather than simple mixing. According to a parallel approach, the free water molecules in the external atmosphere are in equilibrium with the bound water. Since the formation of hydrogen bonds is an exothermic process, the value of the equilibrium constant (α) is decreased by increasing temperature ($d\ln\alpha/dT = \Delta H/RT^2$ where ΔH is the heat of interaction). A decrease in α at higher temperatures leads to a decrease in the equilibrium conversion, which leads to a lower pick-up of water, as was obtained.

The plateau value of Δ (Fig. 8), which is reached at relatively low levels of water vapor (ca. 2000 ppm), and the small change in the value of $1/P^2$ (Fig. 7) (the relative value of $1/P^2$ is dependent on the dimensions of the specimen) indicate that at high humidity there is no significant change in the mass of the specimen -- implying that the observed T_{H_2O} is not due to water condensed on the polymer.

Thermal hysteresis develops in the temperature range -45° to 20°C at low levels (180 ppm) and shifts up to from 4° to 77°C at higher levels (10,000 ppm) of water vapor. A significant change in values of Δ is also observed, i.e., 0.02545 (-4°C, 1.07 Hz) for the former and 0.04495 (52°C, 1.02 Hz) for the latter. As it can be seen from Fig. 6, small changes in the values of $1/P^2$ exist in this region which depend on the direction of temperature change. The hysteresis loop differs from T_{H_2O} (Table 3) in that it increases with the humidity level without reaching a limit, and it is coupled with the water flash-off from the apparatus (Figs. 2 and 6). There-

fore, it is concluded that this hysteresis is due to plasticization of the polymer by water. The shift in the hysteresis region results from elimination of the plasticizing water which occurs at higher temperatures for higher levels of water vapor in the atmosphere.

That the T_{H_2O} transition of the polyimide occurs at a lower temperature (-122°C) than for polymethylmethacrylate (-100°C) suggests that the water bound to a polar site in the rigid polyimide backbone moves more readily (i.e. at lower temperatures) than when bound to the polar site of the ester side group. In polyimide, the water transition is not coupled to an obvious secondary relaxation of the polymer whereas it is presumably coupled to the motions of the ester group in polymethylmethacrylate.

In order to investigate the effect of water vapor on the polyimide quantitatively, the external humidity was increased incrementally and the development of the thermomechanical spectra was followed. A plot of Δ at the maximum of T_{H_2O} vs. the humidity level expressed as ppm_v H_2O in He (Fig. 8), is similar to the plot of amount of gas adsorbed vs. its pressure for the case of one molecule occupying a single site (21, 22).

Assuming that Δ at the peak is proportional to the volume fraction of the lossy part of the solid (23), and using the direct proportionality of level of water vapor (ppm_v H_2O/He) to the partial vapor pressure of water in the gas mixture, Langmuir's equation (21) should be applicable:

$$p/\theta = \frac{1}{a} + p$$

Here, p is the gas pressure, θ the fraction of the occupied sites and a is a factor which is considered to be dependent on the temperature alone and is defined as follows:

$$1/a = \left(K/\delta \quad \sqrt{2MkT}\right) e^{-q/RT}$$

In this, K is a velocity constant of desorption, δ is a probability factor, M is the molecular weight of the adsorbed species, k is the Boltzman constant, T is the temperature in °K, q is the heat of adsorption per gram molecule and R is the gas constant.

If $(\Delta-\Delta_o)$ (for the same specimen) is linearly dependent on the water concentration in the polymer, as assumed, then

$$\theta = \frac{\Delta-\Delta_o}{\Delta_{max}-\Delta_o}$$

where Δ_o and Δ_{max} are the minimum and the maximum values of Δ at T_{H_2O}, respectively.

A plot of H/θ vs. H (humidity level; ppm_v) gives a straight line (Fig. 10) with slope 45°, as expected. The increase of the intercept with the temperature also agrees with the anticipated behavior of $1/a$.

CONCLUSIONS

The present investigation demonstrates the utility of the TBA method in detecting the presence of small amounts of water in polyimide systems. More specific correlations between the peak intensity location (temperature) and molecular architecture of polymers will be sought using systematic series of polymers and reactants.

ACKNOWLEDGMENTS

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TABLE CAPTIONS

Table 1. T_{H_2O} transitions of polymers.

Table 2. Transition temperatures of polyimides.

Table 3. T_{H_2O} transition at different humidity levels after
conditioning at 30°C.

FIGURE CAPTIONS

Fig. 1. Synthesis of Polyimide.

Fig. 2. Temperature and humidity level (expressed as parts per million
of water in helium on a volume basis) for a constant adjustment
of the humidity system vs. time in the TBA system.

Fig. 3. Thermomechanical spectra of polyimide precursor (30°C → 325°C)
and polyimide (325°C → -190°C → 140°C).

Fig. 4. Thermomechanical spectra of polyimide after conditioning in a dry
atmosphere.

Fig. 5. Thermogravimetric analysis of polyimide.

Fig. 6. Thermomechanical spectra of polyimide after conditioning in a
humid atmosphere.

Fig. 7. T_{H_2O} transition after conditioning at 30°C at different humidity
levels.

Fig. 8. Δ at T_{H_2O} vs. humidity level of conditioning atmosphere at 30°C.

Fig. 9. Thermomechanical spectra of polyimide dried after conditioning
in the sequence of humid atmospheres used in the experiments.

Fig.10. Langmuir plots of H/θ vs. H.

TABLE 1. T_{H_2O} Transitions of Polymers

No.	STRUCTURE		T_{H_2O} [°C]	Reference
	Dianhydride	Diamine		
1	(structure)	(structure)	-80 (0.50 Hz)	7
2	(structure)	(structure)	-122 (1.01 Hz)	Present Investigation
3	(structure)	(structure)	-100 (0.90 Hz)	7
4		(structure)	-100 (0.95 Hz)	7
5		(structure)	-90 (0.88 Hz)	7
6	(structure)	(structure)	-100 (0.95 Hz)	7
7		(structure)	-120 (0.96 Hz)	7
8		(structure)	-100 (0.86 Hz)	7
9	Polymethylmethacrylate (atactic)		-103	12,21
10	Epoxies		-90	10
11	Polyaminoacids		-120 -130, 0-35	14

TABLE 2. Transition Temperatures of Polyimides.
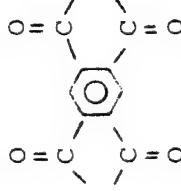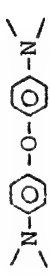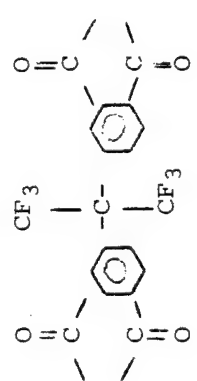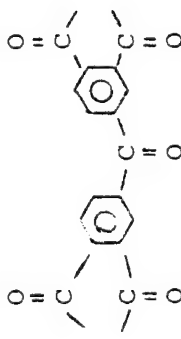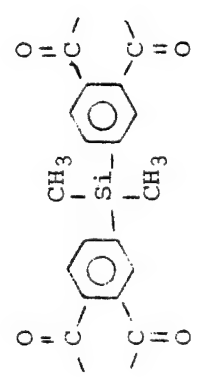
No.	STRUCTURE		TRANSITIONS			Ref.
	Dianhydride	Diamine	T_g (°C)	T_{sec} (°C)	T_{sec}/T_g (°K/°K)	
1	(pyromellitic dianhydride structure)	(oxydianiline diamine structure)	> 330	? 210	< 0.80	7,8
2	(6FDA dianhydride structure with $-C(CF_3)_2-$)		319	140	0.70	Present Investigation
3	(benzophenone-type dianhydride structure)		283	112	0.69	7,8
4	(silicon-containing dianhydride structure with $-Si(CH_3)_2-$)		271	94	0.68	7,8

TABLE 3

T_{H_2O} Transition at Different Humidity Levels after Conditioning at 30°C.

$ppm_v H_2O/He$	T_{H_2O} (°C)	Frequency (Hz)	Δ
20	-118	1.10	0.00854 (Δ_o)
180	-121	1.11	0.02088
385	-120	1.10	0.02529
590	-120	1.10	0.02878
1200	-124	1.12	0.02998
1500	-122	1.10	0.03248
2000	-122	1.12	0.03248
3300	-121	1.11	0.03457
4600	-124	1.11	0.03469
6000	-120	1.10	0.03498
9000	-121	1.10	0.03492
> 10000	-119	1.10	0.03511 (Δ_{max})

Figure 1

Figure 2

LOG Δ

EXPERIMENTAL DETAILS

PRECURSOR : THF (20% BY WEIGHT)

PLOT : 30°C → 325°C → -190°C → 140°C

ATMOSPHERE : 140 PPM$_V$ H$_2$O/He

ΔT/Δt = 1.5°C/MIN.

TRANSITIONS

IMIDIZATION = ~170°C

T_g = 313°C (0.6 Hz)

T_{sec} = 135°C (1.0 Hz)

T_{H_2O} = -117°C (1.1 Hz)

TEMPERATURE, (MV, IRON–CONSTANTAN)

$LOG \dfrac{1}{P^2}$

Figure 3

Figure 4

EXPERIMENTAL DETAILS

CONDITIONING : 325°C / 5 HR / 20 PPM$_V$ H$_2$O / He
PLOT : 325°C → -190°C → 325°C
$\Delta T / \Delta t$ = 1.5°C/MIN.

TRANSITIONS

T_g = 319°C (0.6 Hz)
T_{sec} = 135°C (1.1 Hz)

TEMPERATURE , (MV, IRON –CONSTANTAN)

LOG Δ

LOG $\frac{1}{P^2}$

Figure 5

EXPERIMENTAL DETAILS

CONDITIONING: 325°C/1 HR / 10,000 PPM$_v$ H$_2$O/He

PLOT : 325°C —→ -190°C —→ 325°C

ΔT/Δt = 1.5°C/MIN.

TRANSITIONS

T_g = 319°C (0.6 Hz)
T_{sec} = 135°C (1.1 Hz)
T_{H_2O} = -122°C (1.0 Hz)

LOG Δ

LOG $\frac{1}{P^2}$

TEMPERATURE , (MV , IRON–CONSTANTAN)

Figure 6

Figure 7

Figure 8

LOG Δ

LOG $\frac{1}{P^2}$

TEMPERATURE , (MV, IRON–CONSTANTAN)

EXPERIMENTAL DETAILS

CONDITIONING: 325°C/5 HR/13 PPM$_V$ H$_2$O/He

PLOT: 325°C ⟶ -190°C

ΔT/Δt = 1.5°C/ MIN.

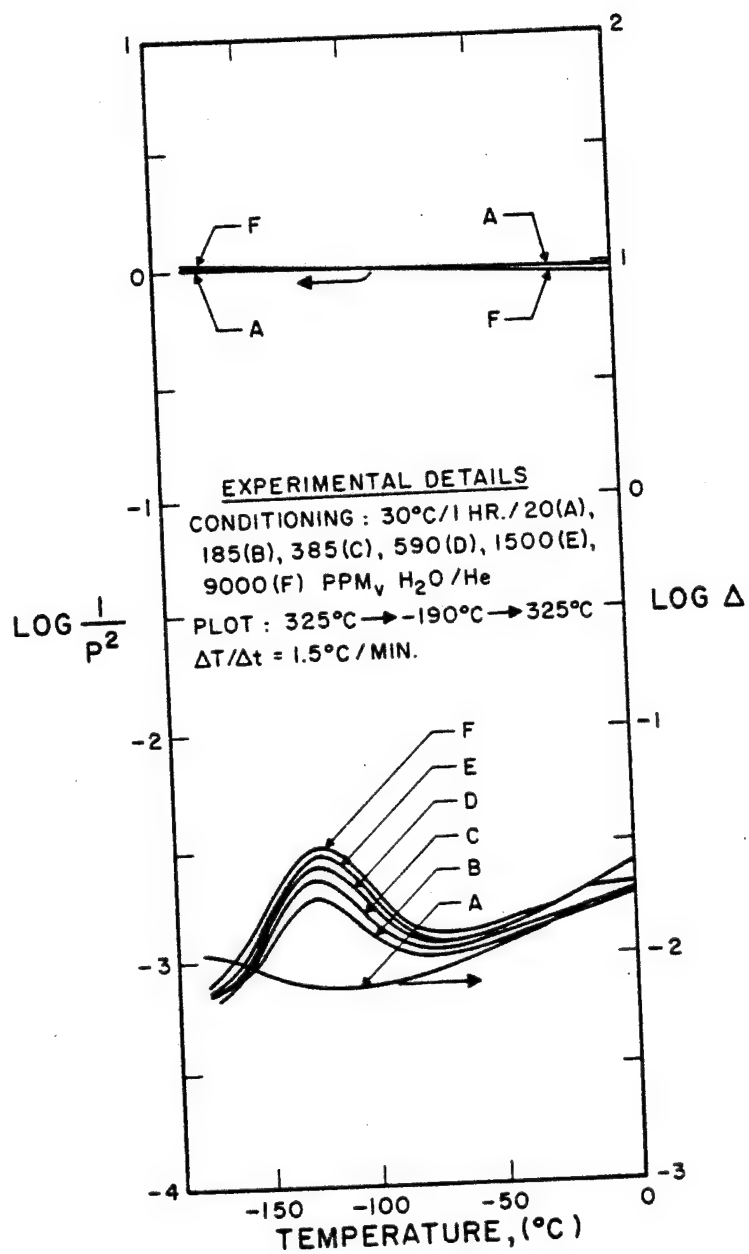TRANSITIONS

T_g = 319°C (0.6 Hz)

T_{sec} = 135°C (1.1 Hz)
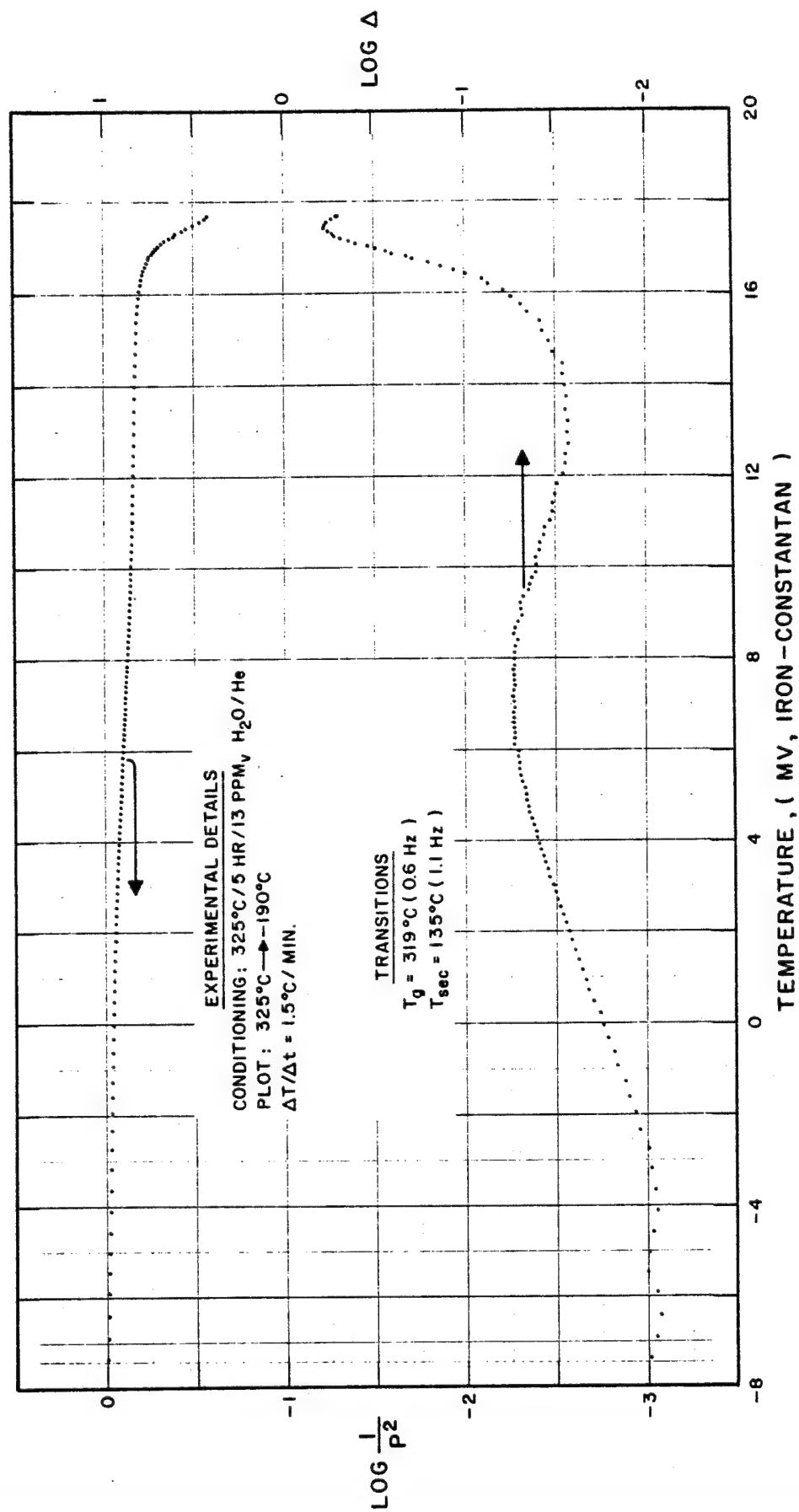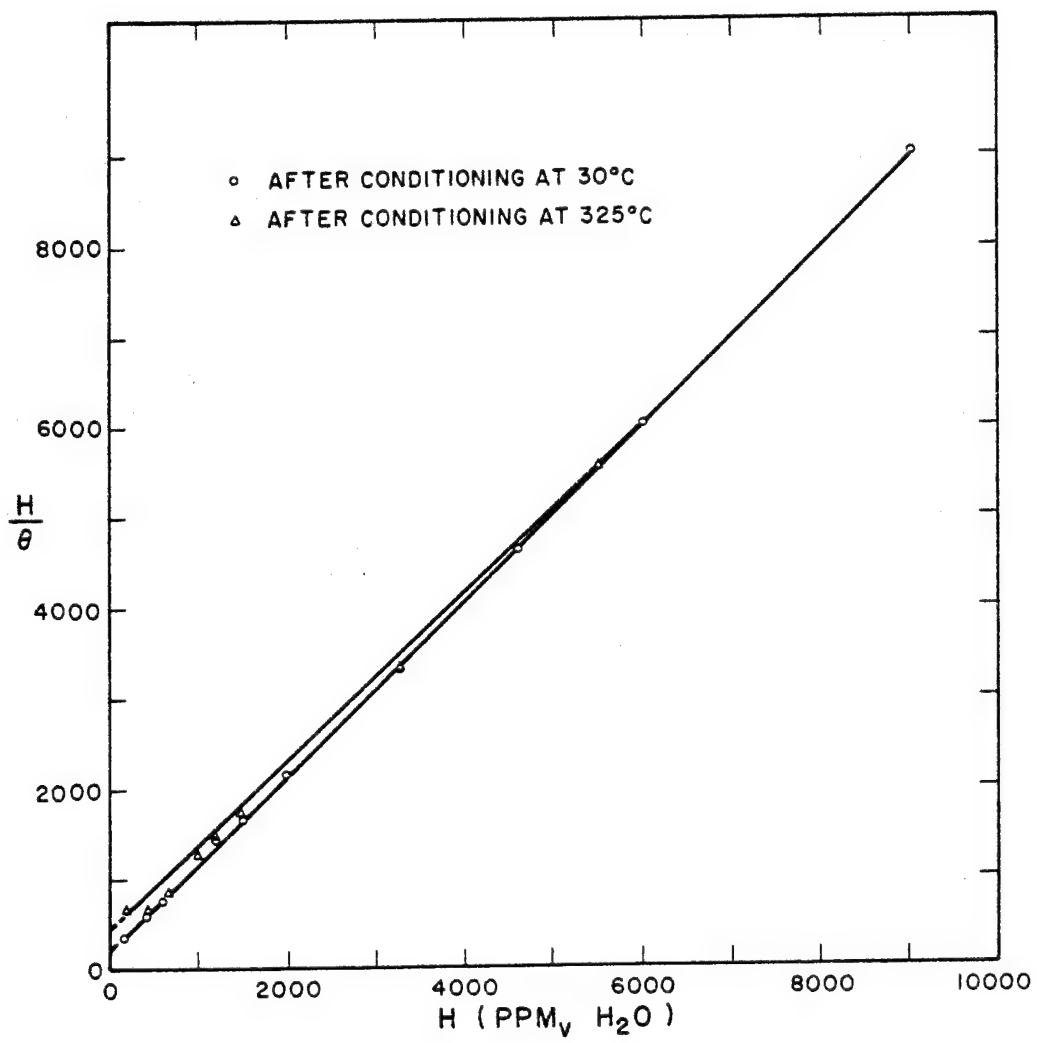
Figure 9

Figure 10

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The effect of water vapor on a polyimide has been investigated in the temperature region -190° to 325°C using an automated torsion pendulum. A damping peak "T_{H_2O}" develops at -122°C (1 Hz) in the thermomechanical spectra of the polymer which is due to water-polymer interactions. The peak intensifies as the humidity of the conditioning atmosphere, at both 30°C and at 325°C, increases and attains a limiting value at about 2000 ppm_V H_2O. The process is reversible. It is concluded that the number of sites in the

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polymer for interaction with water is low and limited (< 0.3 molecules H_2O per polymer repeat unit) and, assuming direct proportionality between the intensity of the loss peak and the amount of water adsorbed, that the adsorption of water vapor follows the Langmuir isotherm.

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